

PHOTOGRAPHIC RESEARCHES ON PHOSPHORESCENT SPECTRA:

ON VICTORIUM, A NEW ELEMENT ASSOCIATED WITH YTTRIUM.¹

IT has long been known that certain substances enclosed in a vacuous glass bulb phosphoresce brightly when submitted to molecular bombardment from the negative pole of an induction coil. The ruby, emerald, diamond, alumina, yttria, samaria and a large class of earthy oxides and sulphides emit light under these circumstances. Examined in a spectroscope the light from some of these bodies gives an almost continuous spectrum, while that from others, such as alumina, yttria and samaria, gives spectra of more or less sharp bands and lines. Since 1879 I have been working on these phosphorescent spectra, chiefly in connection with the earths of the yttria group, and by chemical fractionation I have succeeded in separating from this group bodies whose phosphorescent spectra consist chiefly of single groups of lines, other groups being absent. For the last six years the research has been extended beyond the visible spectrum, and photographs of the ultra-violet portion of the spectra are now being taken with a spectrograph with a complete quartz train. Some of the results of this investigation were exhibited at the soirée of the Royal Society on May 3. A preliminary mention of the discovery of a new element was made in my address to the British Association in September last, when I provisionally called it Monium; but for several reasons I now consider the name Victorium more appropriate.

The complicated scheme of fractionation carried on for so many years is illustrated in the accompanying diagram. This must be considered only as an indication of the methods employed, and not as an actual representation of every operation through which the material has passed. Crude yttria, from samarskite, gadolinite, cerite and other similar minerals, is the raw material. The first operation is to free it roughly from earths of the cerium group—an operation effected by taking advantage of the fact that the double sulphates of potassium and the yttrium metals are easily soluble in saturated potassium sulphate solution, while the corresponding double sulphates of the cerium group of metals are difficultly soluble.

After this preliminary treatment, the crude yttria is converted into nitrate, represented by the topmost circle on the diagram. The nitrate is exposed to heat until it fuses to a clear liquid, care being taken to distribute the heat uniformly through the mass. Presently the liquid mass commences to decompose, giving off red vapours. After this has proceeded for a little time, the fused mass is carefully poured into water, and the liquid well boiled. A white precipitate of basic nitrate forms, while the undecomposed nitrates remain in solution. These are separated by filtration—the precipitate going to the right and the solution to the left. The basic nitrate is dissolved in nitric acid, and the right and left solutions are then evaporated to dryness and fused as before. Partial decomposition by heat again divides each of these portions into two lots, soluble and insoluble. The soluble from the left-hand lot goes still further to the left, and its insoluble portion to the right. The soluble from the right-hand portion goes to the left, where it mixes with the insoluble from the other portion, while its insoluble portion goes still further to the right. This series of operations is continued for as long a time as the material will hold out.² From a description, the process seems to be more complicated than it really is, but a study of the diagram and the direction of the arrows makes it clear. The number of times this operation is performed varies

with each lot of earth fractionated. The portions submitted to fusion rapidly diminish in quantity, and the

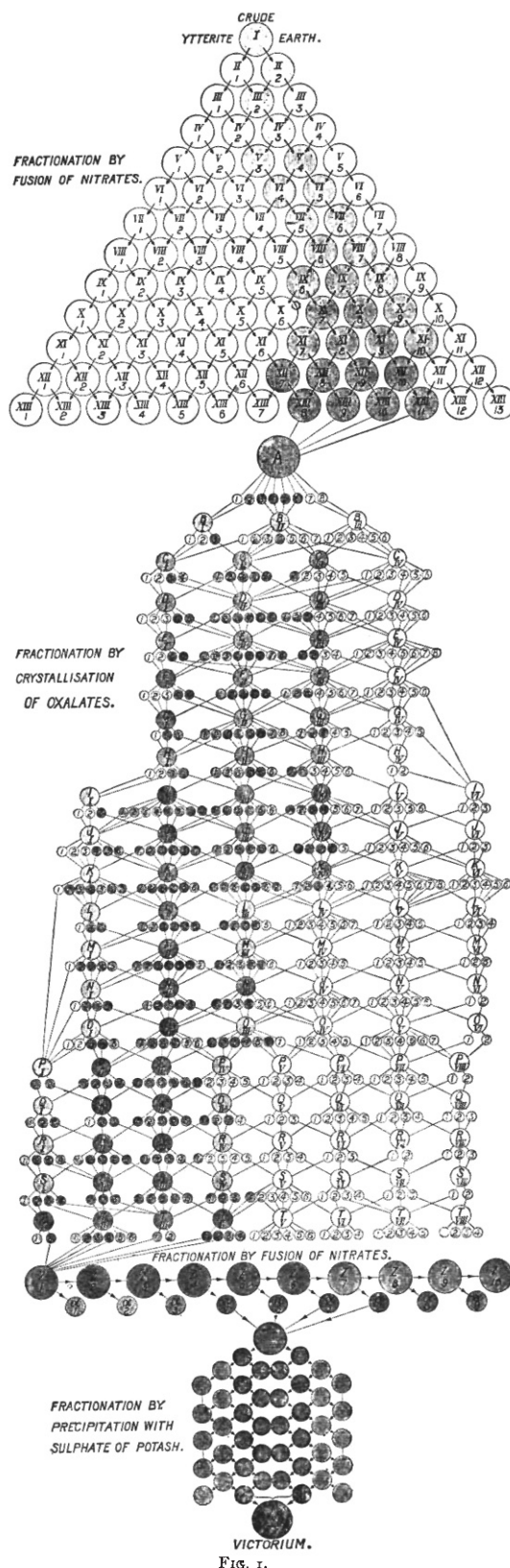


FIG. 1.

¹ A paper read before the Royal Society, May 4, by Sir William Crookes, F.R.S.

² "On the Methods of Chemical Fractionation," British Association, Birmingham Meeting, 1886; *Chemical News*, vol. liv. p. 131.

operation is continued until the material becomes too scanty.

The last horizontal line of fractions, spectroscopically examined in a radiant matter tube, shows differences in the visible spectrum. For many years I recorded these differences in coloured drawings, which have served on several occasions to illustrate papers before this Society.¹ In the year 1893 I commenced to record the differences between the various spectra by photographing them in a spectrograph having a complete quartz train, and since that time attention has chiefly been directed to the variations in the number, character and positions of the lines and bands in the ultra-violet spectrum; these are more striking than those which are visible, and as they are self-recording, results are more rapidly attained. A description of this instrument is given further on.

On placing the photographed spectra of one of the horizontal lines of earths in order, several differences are detected. One striking difference is seen in the behaviour of a group of lines in the ultra-violet. It is nearly absent in the end fractions, gradually becoming stronger towards the middle, and attaining a maximum in the fractions situate about two-thirds towards the right. This shows that at least three different bodies are present: one, the great bulk, having a nitrate difficult to decompose; another, whose nitrate is easiest to decompose; and a third body, occupying an intermediate position, whose nitrate decomposition occurs at temper-

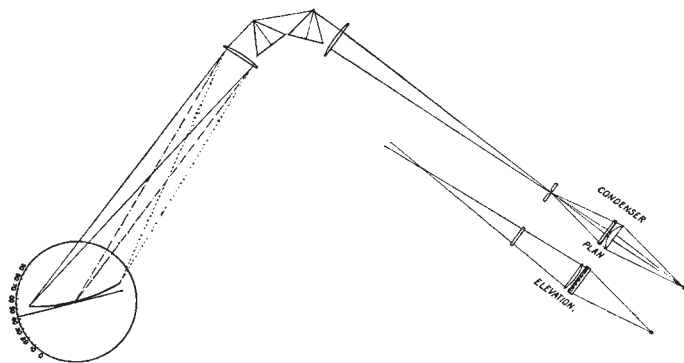


FIG. 2.

atures between that required by the others, but nearer that of the nitrate easiest decomposed.

The above method of fractionation is not so effectual if more than two bodies are present. In that case the process fails, in any reasonable time, to yield practically pure specimens of more than two out of a group of closely allied earths. Thus, if there are three earths—say A, B and C—whose positions in reference to the chemical process employed are in the written order of sequence, we may get a specimen of A as nearly as we please free from B and C, and a specimen of C as nearly as we please free from A and B, but we cannot get a specimen of B practically free from A and C. The law seems to be that to obtain practically pure specimens of three closely allied earths, it is essential to have recourse to at least two different chemical processes. The mere continued repetition of the same process will not do, unless, indeed, the operations are repeated such a vast number of times as to make the approximate expressions no longer applicable, even though the substances are chemically very close.

For this and other reasons it is advisable to change the method of fractionation after one process has been in operation for some time. It is evident that any process of fusion, crystallisation or precipitation can only divide the mass of material into two parts, a soluble and an in-

soluble portion, crystals and mother liquor; and after a time a balance of affinities seems to be established, and further fractionation appears to do little good. It is better then to change the operation.

Following the diagrammatic scheme, the portions of earths containing most victorium are collected together and fractionated by the crystallisation of the oxalates from a solution strongly acidulated with nitric acid in the following manner:—

To a boiling acid solution of the nitrate a small quantity of hot solution of oxalic acid is added. The solution remains clear, and it is only after vigorous stirring that a small quantity of insoluble oxalate is formed. The whole is thrown on a hot-water filter and slightly washed with boiling water. To the boiling filtrate a fresh lot of hot solution of oxalic acid is added, and stirred till more insoluble oxalate comes down. This is again filtered off, and the operations of precipitating, stirring, filtering, and washing are repeated, always keeping the temperature as near the boiling point as possible, until the whole of the earths are precipitated. Generally the initial earth is divided by this method of fractionation into from six to twelve portions. Each of these oxalates is dried, ignited, dissolved in nitric acid, and the above-described operations repeated. Photo-spectroscopic tests are constantly taken during the progress of this fractionation, and portions are mixed together according to the data thus obtained, as shown on the diagram by the lines

joining the fractions. The object being to avoid lateral spreading as much as possible, and, while concentrating the special line-giving earth, to prevent its too great diffusion over a large number of fractions. When the fractionation by the oxalate method has proceeded for a considerable time, the fractions rich in victorium are collected together and submitted to another mode of treatment.

These fractions are converted into nitrates, and a small quantity is thrown out by partial decomposition by heat, according to the method already described. The filtrate is evaporated to dryness and again fused, so as to throw out a little more. This operation is repeated as long as any soluble nitrate is left. Generally from six to twelve portions are thus obtained.

These form a regular series, differing according to the stability of the nitrate under heat. On testing, the victorium is found to concentrate in the centre portions, being less easily decomposed than the earths of the cerium group, and more easily decomposed than those of the yttrium group.

The fractions rich in victorium are converted into sulphates and mixed with a hot saturated solution of potassium sulphate. The precipitate is dissolved in boiling water and mixed with a further quantity of solution of potassium sulphate. This produces a small quantity of a precipitate. The filtrate from the first precipitate is also mixed with fresh potassium sulphate, and the operations are repeated, mixing the centre solutions to one lot and the side solutions to another, as shown by the lines on the diagram. It is found on photo-spectroscopic examination that the earths thrown out on each side are poorest in victorium, whilst those in the middle are richest. After a time no further concentration is effected in this manner, all the earths that can be removed as being more or less soluble in potassium sulphate having been eliminated.

In thus describing the method of fractionation, my object has been not so much to give a description of the plan actually carried out in the laboratory—for the details have varied with each operation—but to give an intelligible idea of the general manner in which a very complicated operation is effected. In the diagram I am supposing that one particular substance, victorium, is to

¹ On some New Elements in Gadolinite and Samarskite Detected Spectroscopically" (*Roy. Soc. Proc.*, No. 245, 1886 vol. xl. p. 502).

be separated, and I have endeavoured to show its migrations and gradual concentration as the work progresses, by tinting the fractions where it mostly would concentrate, the depth of tint representing the amount of concentration.

In the purest condition yet obtained victoria is an earth of a pale brown colour, easily soluble in acids. It is less basic than yttria and more basic than most of the earths of the terbia group. In chemical characters it differs in many respects from yttria. From a hot nitric acid solution victorium oxalate precipitates before yttrium oxalate and after terbium oxalate. On fractional precipitation with potassium sulphate the double sulphate of victorium and potassium is seen to be less soluble than the corresponding yttrium salt, and more soluble than the double sulphates of potassium and the terbium and cerium groups. Victorium nitrate is a little more easily decomposed by heat than yttrium nitrate, but the difference is not sufficient to make this reaction a good means of separating victorium and yttrium. Fusing the nitrates can, however, be employed advantageously to separate mixed victoria and yttria from the bulk of their associated earths.

On the assumption that the oxide has the composition Vc_2O_3 , the atomic weight of victorium is apparently not far from 117.

The photographed phosphorescence spectrum of victoria consists of a pair of strong lines at about λ 3120 and 3117; other fainter lines are at 3219, 3064, and 3060. Frequently the pair at 3120 and 3117 merge into one, but occasionally I have seen them quite distinct. The presence or absence of other earths has much influence on the sharpness of lines in phosphorescent spectra, and it is probable that these lines will be sharp and distinct when victoria is obtained quite free from its associates.

The best material for phosphorescing in the radiant matter tube is not the earth itself, but the anhydrous sulphate formed by heating the earth with strong sulphuric acid and driving off the excess of acid at a red heat. The sulphate thus produced, probably also containing some basic sulphate, is powdered and introduced into a bulb tube furnished with a quartz window, and a pair of thick aluminium poles sealed into the glass with stout platinum wires. The tube is well exhausted, keeping the current from a good induction coil going all the time. The pumping and sparking must continue until the earth glows with a pure light free from haze or cloudiness, and continues so to glow during the passage of the current without deterioration. The exposure in the spectrograph usually occupies an hour.

I give a diagrammatic plan of the two-prism spectrograph used in this research. It is furnished with two quartz prisms, quartz lenses and condensers. The slit jaws are of quartz, cut and polished according to the method I described in the *Chemical News*, vol. lxxi. p. 175, April 11, 1895.

The prisms are made in two halves according to Cornu's plan, one half of each being right-handed and the other half left-handed. One of the lenses also is right-handed and the other left-handed. By this device the effect of double refraction is so completely neutralised that with a five-prism instrument it is impossible, under high magnifying power, to detect any duplication of the lines.

The lenses are each of 52 mm. diameter and 350 mm. focus. The focus of the least refrangible rays is longer than that of the most refrangible rays, and the sensitive film must therefore be set at an angle to get the extreme rays into focus at the same time. But this alone is not sufficient. The focal plane is not a flat surface, but is curved, and the film must therefore be curved,¹ and it is only when both these conditions are fulfilled that perfectly

sharp images of spectral lines extending from the red to the high zinc line 2138.30 can be photographed on the same surface. Celluloid films are used, glass not being sufficiently flexible.

Using the middle position showing the whole spectrum on a plate, the angle is 40° , and the curvature is 190 mm. radius.

The condensers are of quartz, and are plano-cylindrical—one being double the focus of the other. The object of this, when spark-spectra are being photographed, is to concentrate on the slit a line instead of a point of light, as would be the case if ordinary lenses were used.

When photographing phosphorescent spectra—or, in fact, any spectra the wave-lengths of which are either unknown or require verification—I always photograph on the same film a standard spectrum, usually of an alloy of equal molecular weights of zinc, cadmium, tin and mercury. This forms a hard, somewhat malleable alloy, giving throughout the whole photographic region lines the wave-lengths of which are well known. The chief objection to this alloy is its volatility, the poles requiring frequent adjustment. Recently I have used pure iron for this purpose; this has the advantages of giving a great number of fine lines whose wave-lengths are accurately known, and not being very volatile, the poles do not rapidly wear away. If the poles are kept about 1 mm. apart, there is little or no interference from air lines.

The most simple method of applying the standard lines to an unknown spectrum is by the successive employment of two slightly overlapping diaphragms immediately behind the slit, one being used for the experimental and the other for the standard spectrum. In this way, without disturbing the instrument, the two spectra can be recorded on the plate one over the other; the overlap of 1 mm. being in the optical centre of the train. The resulting negative is then transferred to a micrometer measuring machine of special construction, having a screw of 1/100th of an inch pitch, and a means of accurately determining 1/1000th of its revolution, thus measuring directly to the 100/1000th of an inch. In this way, in a five-prism spectrograph having lenses 700 mm. focus, it is possible to determine wave-lengths of photographed lines to the sixth figure.

MATHEMATICS OF THE SPINNING-TOP.¹

I.

“TO those who study the progress of exact science, the common spinning-top is a symbol of the labours and the perplexities of men who had successfully threaded the mazes of the planetary motions. The mathematicians of the last century, searching through nature for problems worthy of their analysis, found in the toy of their youth ample occupation for their highest mathematical powers.

“No illustration of astronomical precession can be devised more perfect than that presented by a properly balanced top, but yet the motion of rotation has intricacies far exceeding those of the theory of precession.

“Accordingly we find Euler and D'Alembert devoting their talent and their patience to the establishment of the laws of the rotation of solid bodies. Lagrange has incorporated his own analysis of the problem with his general treatment of mechanics; and since his time Poinsoth has brought the subject under the power of a more searching analysis than that of the calculus, in which ideas take the place of symbols, and intelligible propositions supersede equations” (Maxwell—“Collected Works,” I. p. 248).

Newton also cites the top as affording an experimental verification of his First Law of Motion—Lex. I. “. . .

¹ “Ueber die Theorie des Kreisel.” F. Klein und A. Sommerfeld. Heft i. ii. Pp. 196 and 197 to 512. (Leipzig: Teubner, 1897-3.)

¹ *Chemical News*, vol. lxxii. p. 87, August 23, 1895; and vol. lxxiv. p. 259, November 27, 1896.